Electronic Supporting Information

Rhenium-catalyzed deoxydehydration of renewable triols derived from sugars

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Contents

1.0 General remarks

All reactions were carried out in dried glassware or hastelloy autoclave vessel with magnetic stirring under aerobic conditions or hydrogen atmosphere. Commercially available chemicals and solvents were purchased from Sigma Aldrich, ABCR and TCI as reagent grade chemicals and were used as received. Rhenium(VII) oxide was stored in the glovebox in order to avoid the formation of perrhenic acid. The deoxydehydration reactions were performed in pressure vials. The yields and conversions were calculated by NMR using dimethyl phthalate as an internal standard in CD_3OD. ^1H and ^{13}C NMR spectra were recorded on Bruker AV 300 or 400 NMR spectrometer. All chemicals shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are related to residual solvent peaks. All spectra were recorded at room temperature unless otherwise specified.

2.0 General procedures

2.1 Hydrogenation of HHD

A 300 mL hastelloy autoclave vessel equipped with a magnetic stirrer was charged with HHD (**2**) (1.00 g, 7.69 mmol) and Ru-MACHO-BH (cat **I**) (23 mg, 0.5 mol%). The contents were dissolved in *i*PrOH (20 mL), the vessel was flushed three times with N_2 and subsequently with H_2, the reactor was pressurized to with H_2 (30 bar) and the reaction mixture was stirred and heated to 100 ^oC for 18 h. After cooling to room temperature and depressurizing the vessel, the resulting yellow solution was filtered through silica and evaporated to dryness to afford the desired product as yellowish oil (1.01 g, 98%)

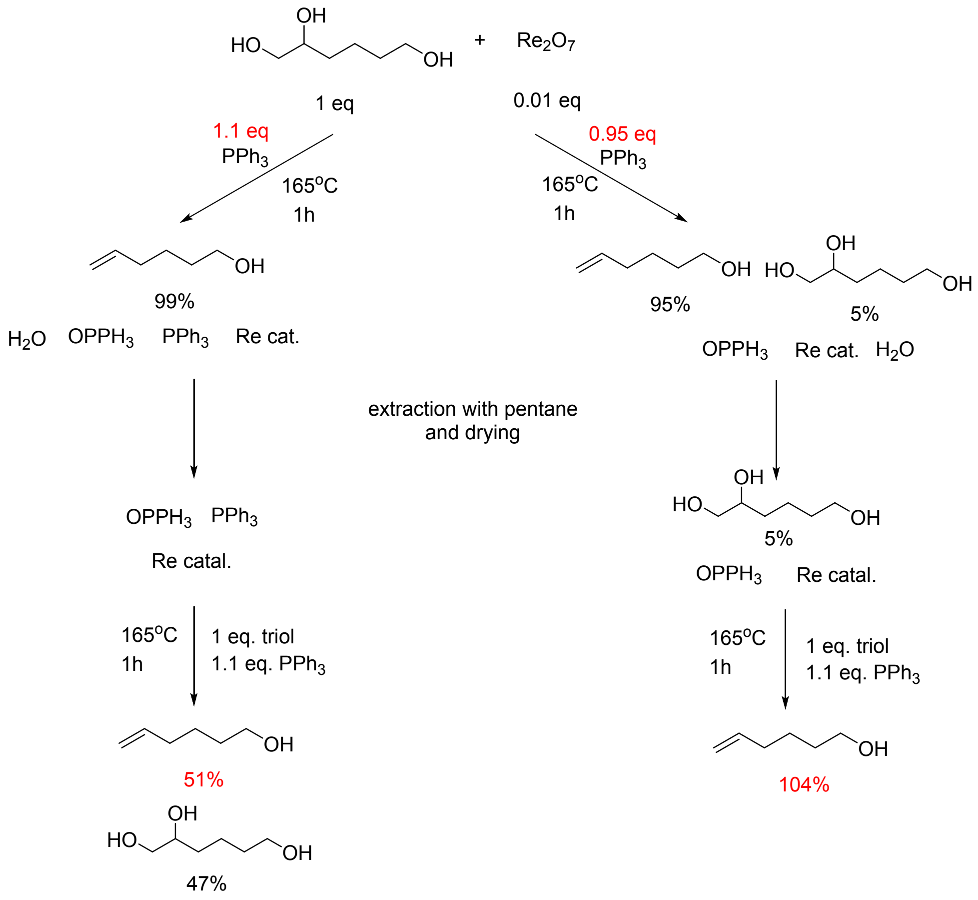
2.2 Screening of Re sources in DODH

Under ambient conditions 1,2,6 hexanetriol (134 mg, 1.00 mmol) and triphenylphosphine (288 mg, 1.10 mmol) were added to a pressure vial which was already charged with the corresponding rhenium catalyst. The reactions were stirred and heated to 165^{o}C for one hour. After cooling to room temperature, CD_3OD (0.6 mL) and dimethyl phthalate (33 µL, 0.20 mmol) were added. The content was filtered through a short plug of silica and yield was calculated by NMR.

2.3 Screening of reducing agents in DODH

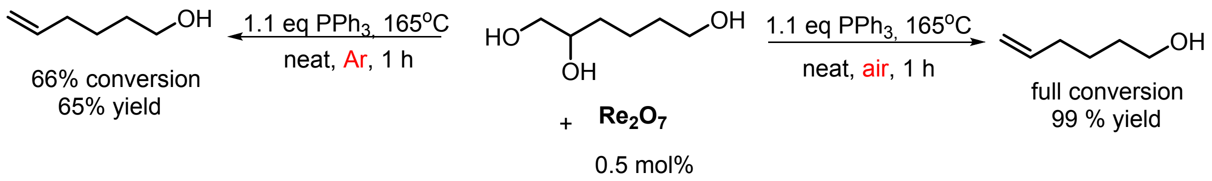
Under ambient conditions 1,2,6 hexanetriol (134 mg, 1.00 mmol) and corresponding reducing agent (2.00 mmol) were added to a pressure vial which was already charged with Re_2O_7 (2.4 mg, 0.005 mmol). The reactions were stirred and heated to 165^{o}C for one hour. All the yields were calculated using procedure described in the section 2.2. The same reactions were performed in hastelloy autoclave when H_2 (7 bar) or CO (7 bar) was used as a reductant.

2.4 Recycle experiments



Under ambient conditions 1,2,6 hexanetriol (134 mg, 1.00 mmol) and triphenylphosphine (288 or 249 mg, respectively 1.10 and 0.95 mmol) (2.00 mmol) were added to a pressure vial which was already charged with Re_2O_7 (4.8 mg, 0.01 mmol). The reactions were stirred and heated to 165°C for one hour. After cooling to room temperature, the vial was washed 5 times with pentane (1 mL) in order to extract 5-hexen-1-ol. The remaining solid- mixture of PPh_3O, PPH_3 and catalyst (PPh_3O, catalyst and 5% 1,2,6-hexanetriol when 0.95 mmol of PPH_3 was used) was dried under vacuum and directly used in the next cycle. After addition of a new portion of 1,2,6-hexanetriol (134 mg, 1.00 mmol) and triphenylphosphine (288 mg, 1.10 mmol) the vial was heated again to 165°C for one hour. All the yields were calculated using procedure described in the section 2.2

2.5 Reaction under inert conditions



Under inert atmosphere and optimized reaction conditions: 1,2,6-hexanetriol (134 mg, 1.00 mmol), triphenylphosphine (288 mg, 1.10 mmol) and Re_2O_7 (2.4 mg, 0.005 mmol) reaction was stirred and heated to 165°C for one hour. NMR studies revealed 65% yield to the corresponding unsaturated alcohol compare to 99% when the pressure vial was charged under aerobic conditions.

2.6 Catalytic DODH of 1,2,5-hexanetriol

Under ambient conditions 1,2,5 hexanetriol (134 mg, 1.00 mmol) and triphenylphosphine (288 mg, 1.10 mmol) were added to a pressure vial charged with Re_2O_7. The reactions were stirred and heated to 165°C for one hour. All the yields were calculated using procedure described in the section 2.2.

2.7 Cyclization of 1,2,5-hexanetriol

Under ambient conditions 1,2,5 hexanetriol (134 mg, 1.00 mmol) was added to a pressure vial charged with catalyst (0.005 mmol) . The contents were stirred and heated to 165°C for ten minutes. All the yields were calculated using procedure described in the section 2.2.

2.8 Deoxydehydration-hydrogenation reaction of 1,2,6-hexanetriol

A 300 mL hastelloy autoclave vessel equipped with a magnetic stirrer was charged with 1,2,6-hexanetriol (134 mg, 1.00 mmol), Re_2O_7 (24 mg, 0.05 mmol) and a co-catalyst (if any was used). The content was dissolved in the corresponding amount of THF, the vessel was flushed three times with N_2 and subsequently with H_2. After flushing, the reactor was pressurized to with H_2 (30 bar) and the reaction mixture was stirred and heated to 165 °C for 5 h. After cooling to room temperature and depressurizing, the reaction mixture was filtered through short plug of silica and the volatiles were removed under reduced pressure. All the yields were calculated using procedure described in the section 2.2.

3.0 Isolation procedures

3.1 Re_2O_7-catalyzed synthesis of unsaturated alcohols from triols

Under ambient conditions the corresponding triol (5.00 mmol) and PPh_3 (1443 mg, 5.50 mmol) were added to the pre-weighted amount of Re_2O_7. The reactions contents were stirred and heated to 165°C until complete conversion of the substrate was achieved. After cooling to room temperature the reaction flask was directly connected to Kugelrohr and the desired unsaturated alcohol was purified by distillation. All products were obtained as colorless liquids.

3.2 Synthesis of 5-methyltetrahydrofurfuryl alcohol

Under ambient conditions 1,2,5 hexanetriol (134 mg, 1.00 mmol) was added to a pressure vial vial which was already charged with Re_2O_7 (2,4 mg, 0.005 mmol) . The reaction was stirred and heated to 165°C for ten minutes. After cooling to room temperature, the content was dissolved in EtOH (1 mL), filtrated through short plug of silica and volatiles removed under reduced pressure to afford desired product as yellow liquid (104 mg, 90%).

3.3 Synthesis of 1-hexanol from 1,2,6-hexanetriol

A 300 mL hastelloy autoclave vessel equipped with a magnetic stirrer was charged with 1,2,6-hexanetriol (670 mg, 5.00 mmol), Re_2O_7 (120 mg, 0.25 mmol) and 5% Pd/C (100 mg). The content was dissolved in THF (50 mL), the vessel was flushed three times with N_2 and subsequently with H_2, the reactor was pressurized to with H_2 (30 bar) and the reaction mixture was stirred and heated to 165 °C for 5 h. After cooling to room temperature and depressurizing the vessel, the reaction mixture was filtered through short plug of silica and volatiles were removed under reduced pressure. The resulting colorless oil was then purified by column chromatography (SiO_2; ethyl acetate:cyclohexane 1:2), yielding 1-hexanol (303 mg, 55%).

4.0 Analytical data of isolated products

1,2,5-hexanetriol (3, mixture of isomers) ^{1}H NMR (300 MHz, MeOD) δ = 5.37-4.56 (brs, 3H), 3.78-3.69 (m, 1H), 3.62-3.54 (m, 1H), 3.51-3.40 (m, 2H), 1.69-1.53 (m, 2H), 1.53-1.31 (m, 2H), 1.18 (d, *J*= 6.3 Hz, 3H) ppm. ^{13}C NMR (75 MHz, MeOD) δ = 73.3, 73.1, 68.7, 68.4, 67.3, 67.2, 36.1, 36.0, 30.7, 30.6, 23.6, 23.5 ppm.

5-hexene-1-ol (5) ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.70 (ddt, J_1= 16.9 Hz, J_2= 10.3 Hz, J_3= 6.6 Hz, 1H), 4.94-4.81 (m, 2H), 3.76 (brs, 1H), 3.47 (t, *J*= 6.6 Hz, 2H), 2.01-1.92 (m, 2H), 1.51-1.28 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.5, 114.3, 62.0, 33.4, 31.9, 25.0 ppm.

3-butene-1-ol (11a) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.70 (ddt, J_1= 17.1 Hz, J_2= 10.3 Hz, J_3= 6.9 Hz, 1H), 5.14-5.05 (m, 2H), 3.63 (q, *J*= 6.1 Hz, 2H), 2.23 (q, *J*= 6.6 Hz, 2H), 2.12 (brs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.0, 117.5, 61.6, 37.1 ppm.

3-butene-2-ol (11b) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.86 (ddd, J_1= 16.1 Hz, J_2= 10.4 Hz, J_3= 5.7 Hz, 1H), 5.16 (dt, J_1= 17.3 Hz, J_2= 1.5 Hz, 1H), 5.01 (dt, J_1= 10.5 Hz, J_2= 1.4 Hz, 1H), 4.29-4.20 (m, 1H), 2.39 (brs, 1H) 1.22 (d, *J*= 6.5 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.4, 113.6, 68.9, 23.0 ppm.

2-butene-1-ol (11c, *Z* isomer) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.60-5.51 (m, 2H), 4.15 (d, *J*= 4.3 Hz, 2H), 2.30 (brs, 1H) 1.62 (d, *J*= 4.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 129.4, 126.9, 58.1, 13.0 ppm.

2-butene-1-ol (11c, *E* isomer) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.71-5.60 (m, 2H), 4.01 (d, 5.0 Hz, 2H), 2.30 (brs, 1H), 1.66 (d, *J*= 5.5 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 130.3, 127.9, 63.5, 17.7 ppm.

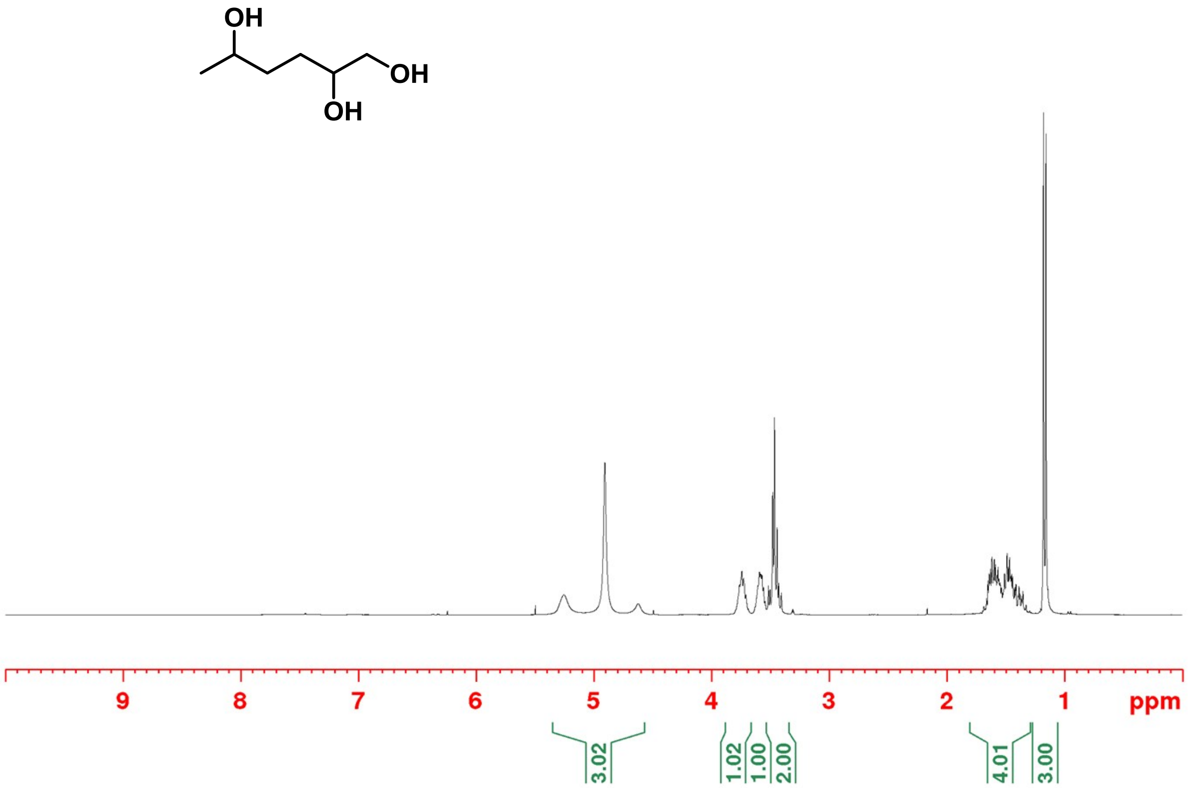
4-pentene-1-ol (11d) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.81 (ddt, J_1= 16.9 Hz, J_2= 10.2 Hz, J_3= 6.6 Hz, 1H), 5.03 (dq, J_1= 17.1 Hz, J_2= 1.6 Hz, 1H), 4.96 (dq, J_1= 10.2 Hz, J_2= 1.2 Hz, 1H), 3.63 (q, *J*= 6.6 Hz 2H), 2.16-2.08 (m, 2H), 1.91 (t, *J*= 5.4 Hz, 1H), 1.69-1.61 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.4, 115.0, 62.4, 33.4, 31.8, 30.2 ppm.

7-octene-1-ol (11e) ^{1}H NMR (400 MHz, MeOD) δ = 5.83 (ddt, J_1= 17.0 Hz, J_2= 10.2 Hz, J_3= 6.7 Hz, 1H), 5.04-4.92 (m, 2H), 4.91 (brs, 1H), 3.56 (t, *J*= 6.6 Hz 2H), 2.13-2.01 (m, 2H), 1.61-1.51 (m, 2H), 1.48-1.31 (m, 6H) ppm. ^{13}C NMR (100 MHz, MeOD) δ = 139.9, 114.8, 62.8, 34.8, 33.5, 30.0, 30.0, 26.7 ppm.

9-decene-1-ol (11f) ^{1}H NMR (400 MHz, MeOD) δ = 5.82 (ddt, J_1= 17.0 Hz, J_2= 10.3 Hz, J_3= 6.7 Hz, 1H), 5.04-4.91 (m, 2H), 4.91 (brs, 1H), 3.56 (t, *J*= 6.7 Hz 2H), 2.11-2.02 (m, 2H), 1.62-1.49 (m, 2H), 1.47-1.29 (m, 10H) ppm. ^{13}C NMR (100 MHz, MeOD) δ = 139.9, 114.8, 62.9, 34.9, 33.6, 30.6, 30.6, 30.2, 30.1, 26.9 ppm.

5-methyltetrahydrofurfuryl alcohol (9, mixture of isomers) ^{1}H NMR (300 MHz, MeOD) δ = 4.16-3.89 (m, 2H), 3.53-3.47 (m, 2H), 2.12-1.88 (m, 2H), 1.80-1.63 (m, 1H), 1.55-1.38 (m, 1H), 1.21 (t, *J*= 6.2 Hz, 3H) ppm. ^{13}C NMR (75 MHz, MeOD) δ = 81.2, 80.6, 77.3, 76.6, 65.9, 65.6, 34.7, 33.8, 29.1, 28.7, 21.4, 21.2 ppm.

hexane-1-ol (13) ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.94 (brs, 1H), 3.56 (t, *J*= 6.7 Hz, 2H), 1.62-1.51 (m, 2H), 1.44-1.28 (m, 6H), 0.94 (t, *J*= 7.0 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 61.6, 32.4, 31.6, 25.4, 22.5, 13.3 ppm.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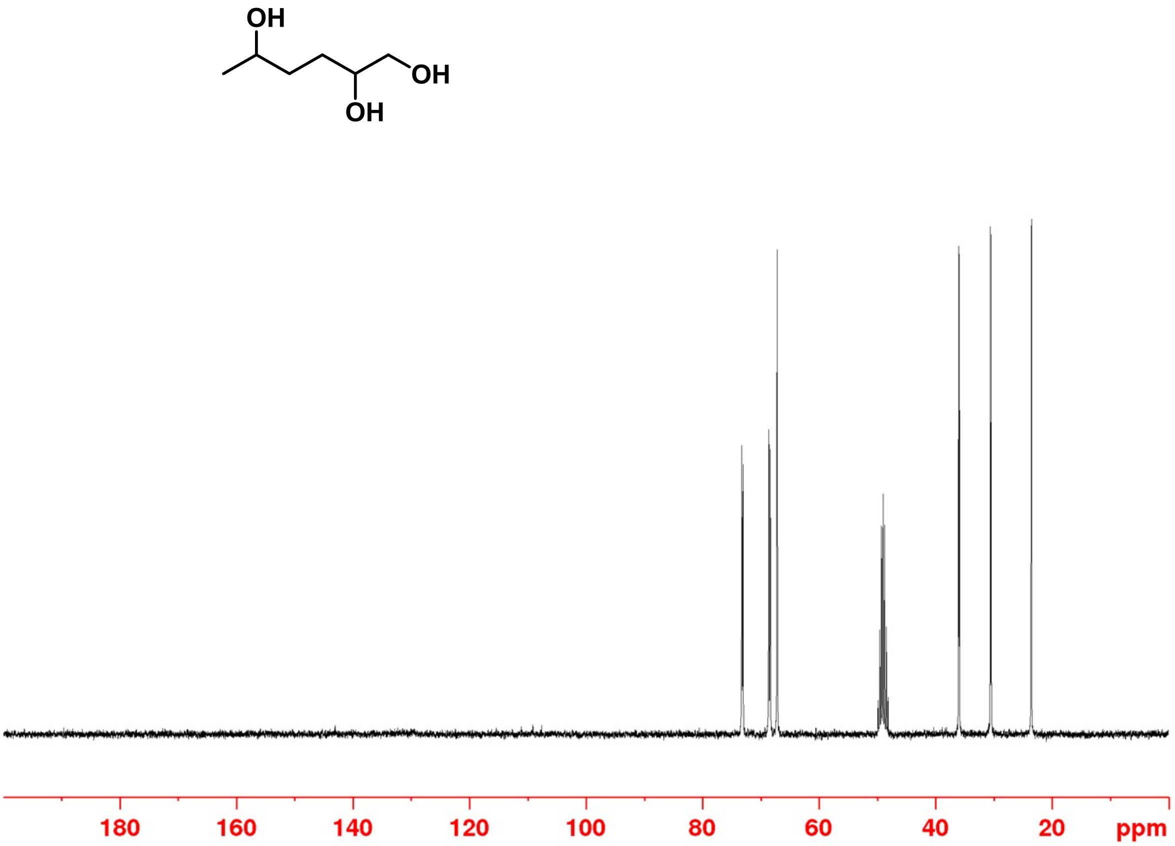
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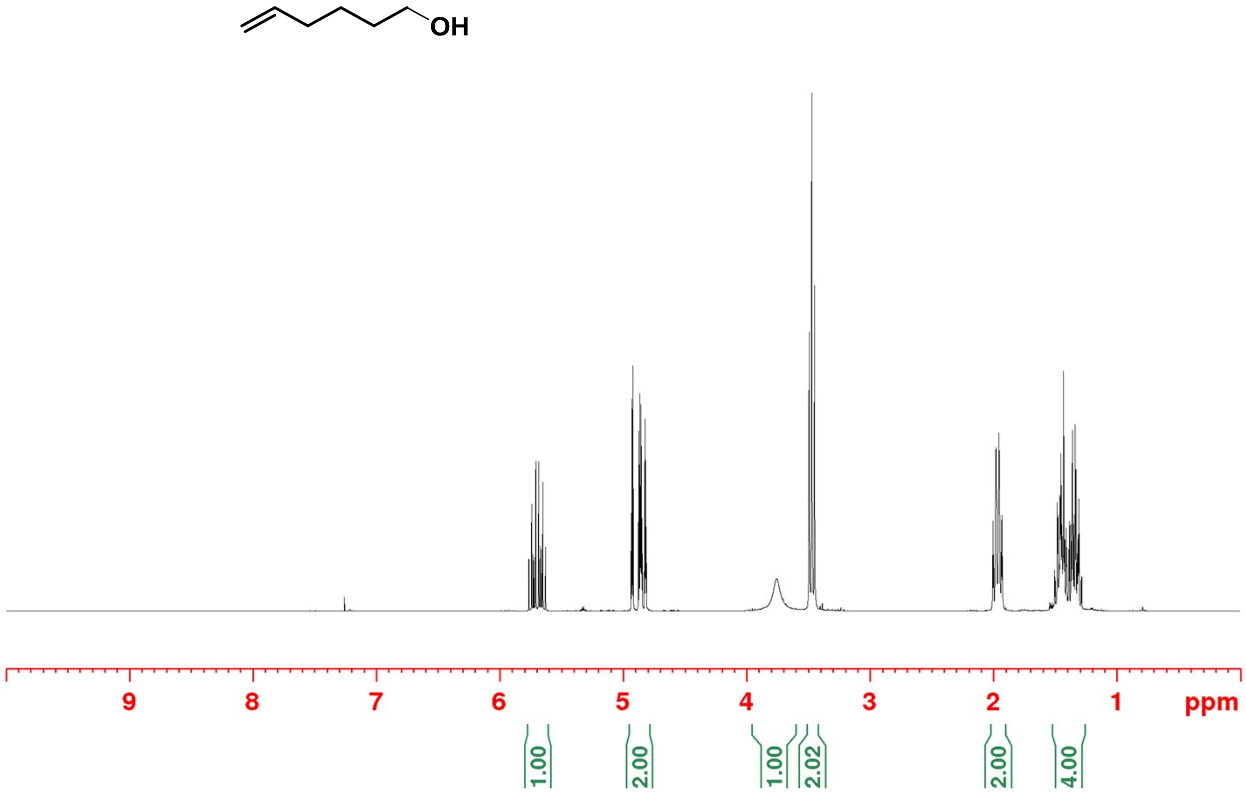
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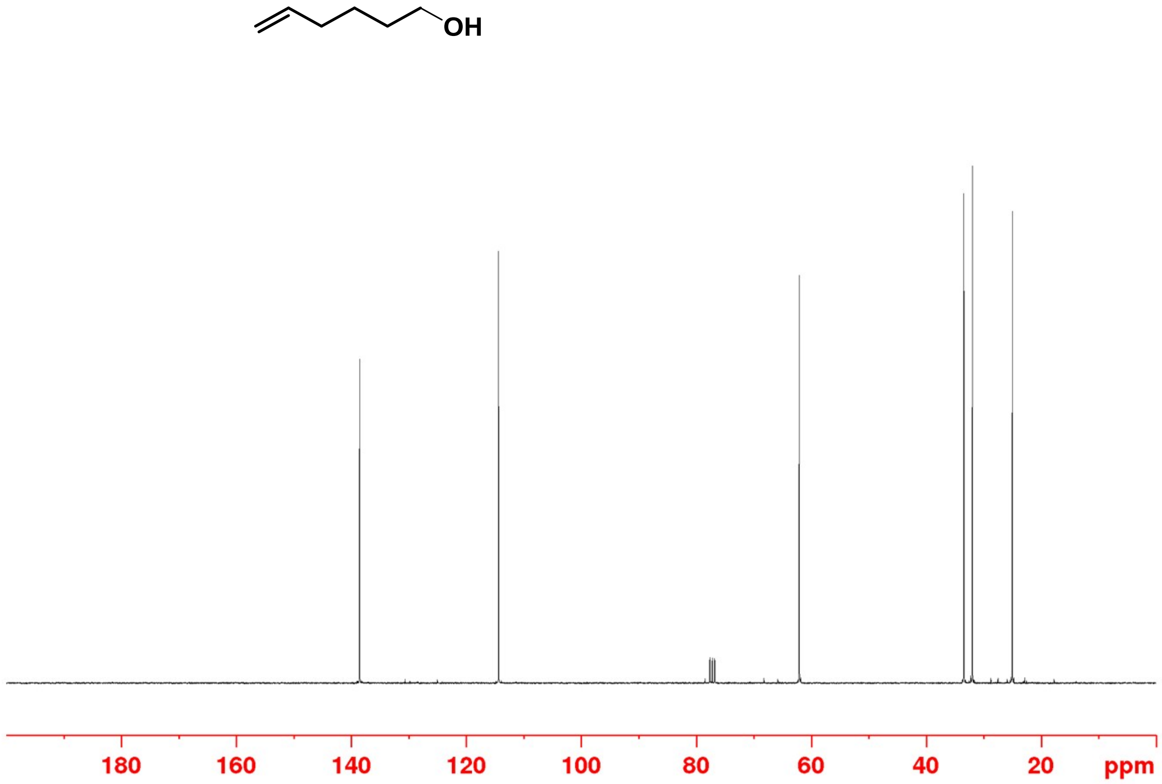
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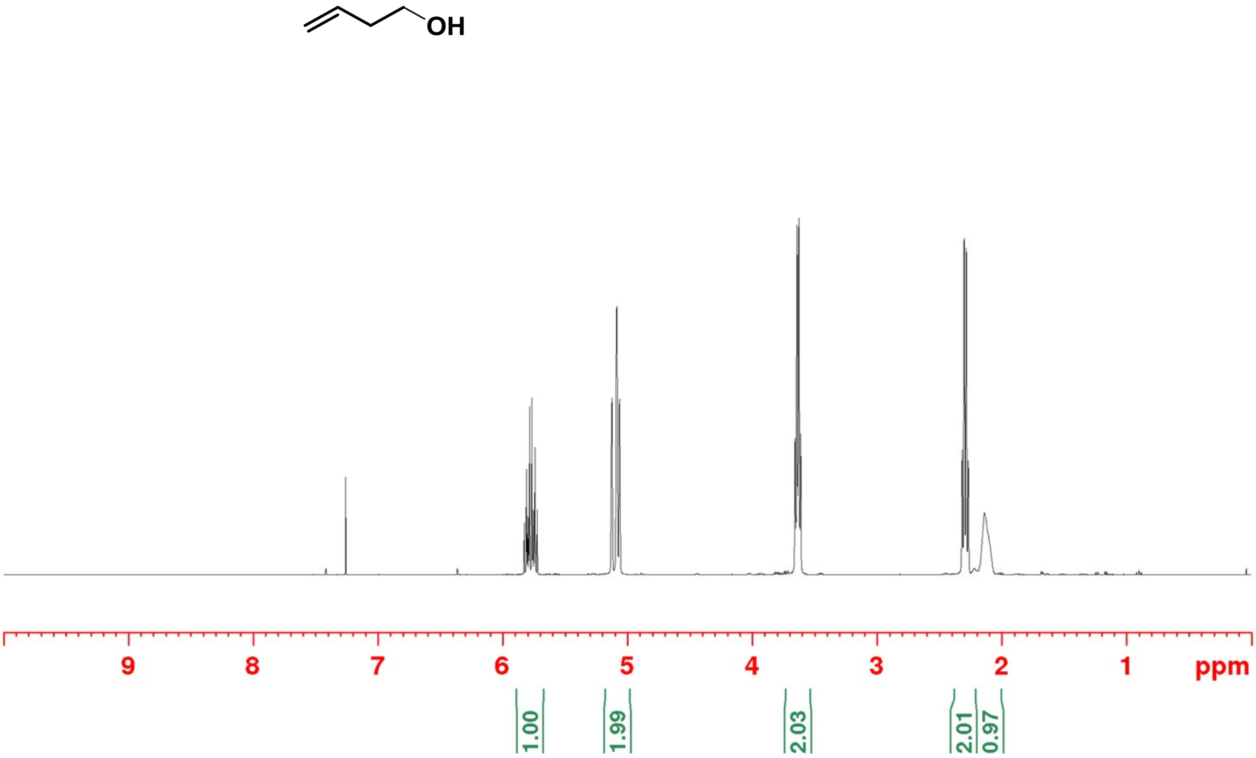
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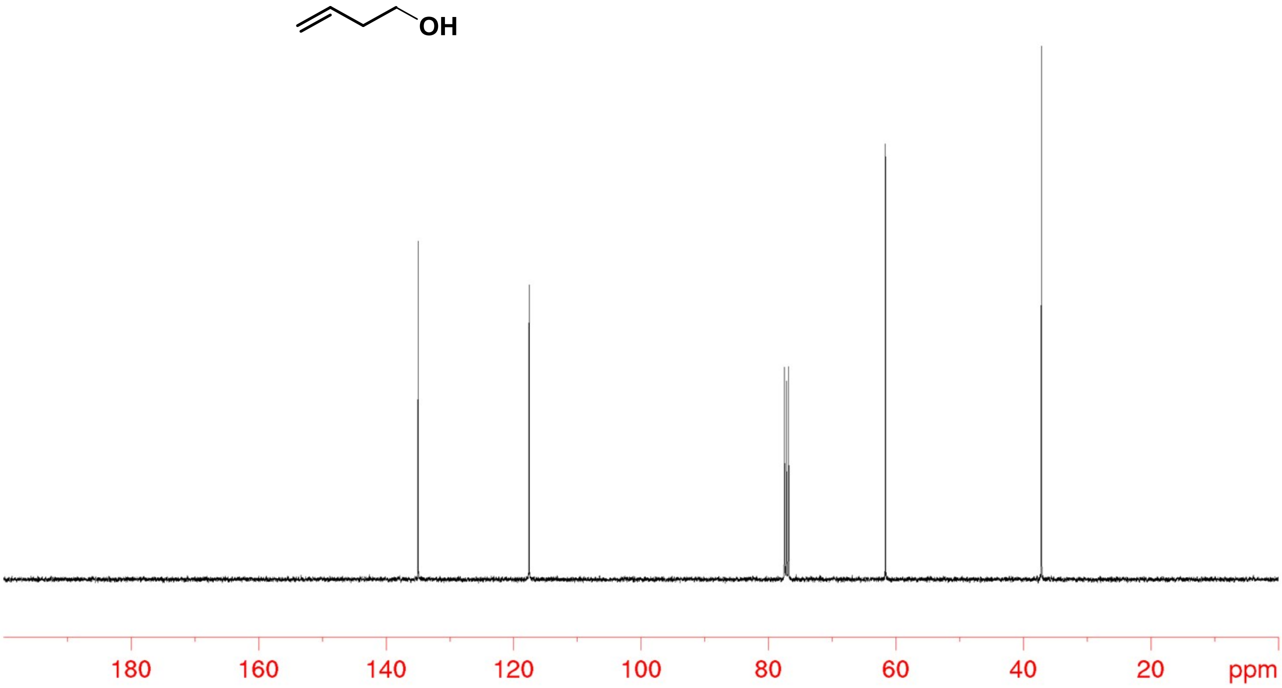
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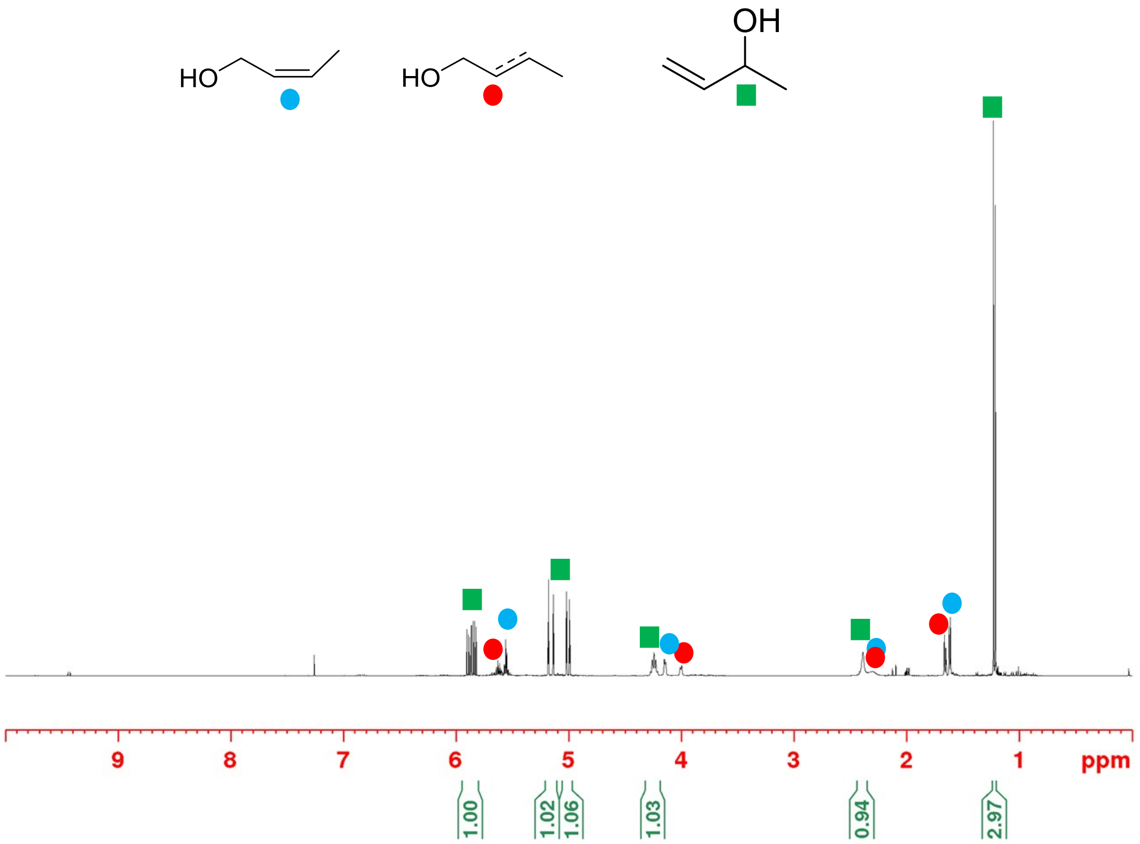
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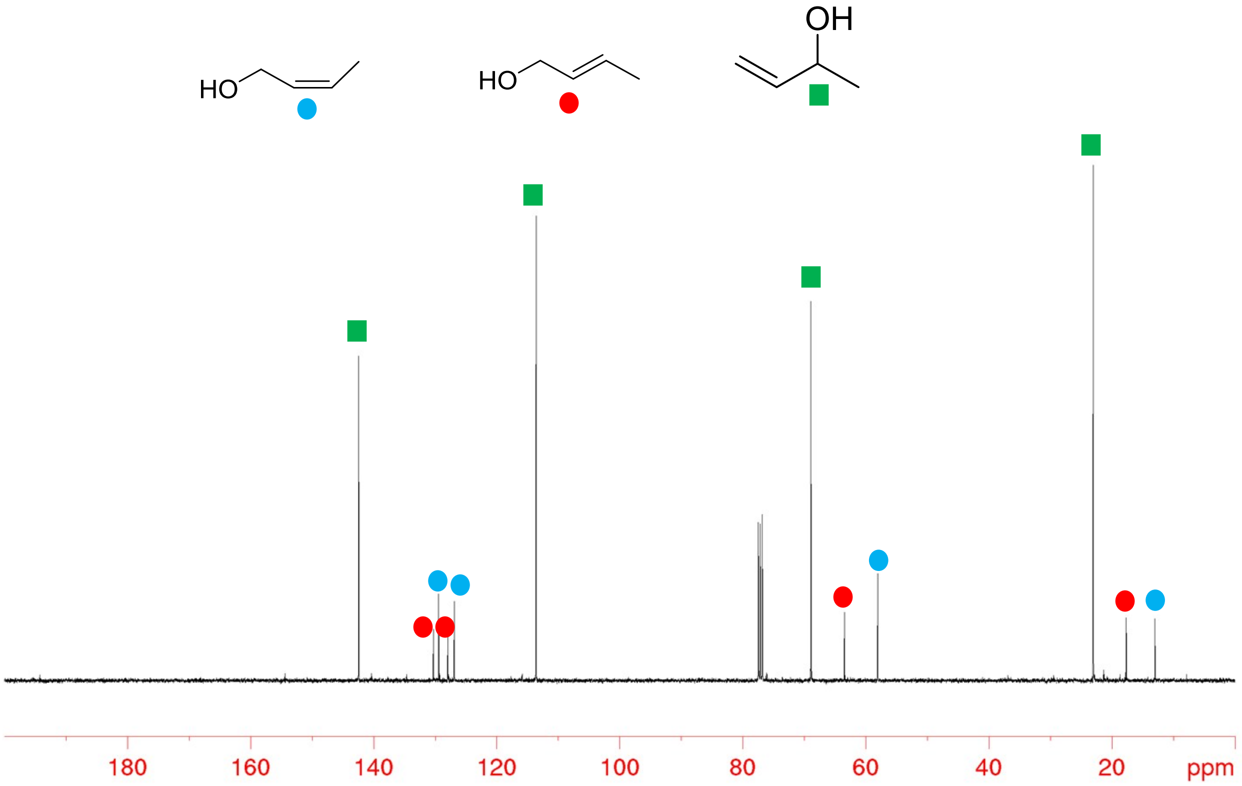
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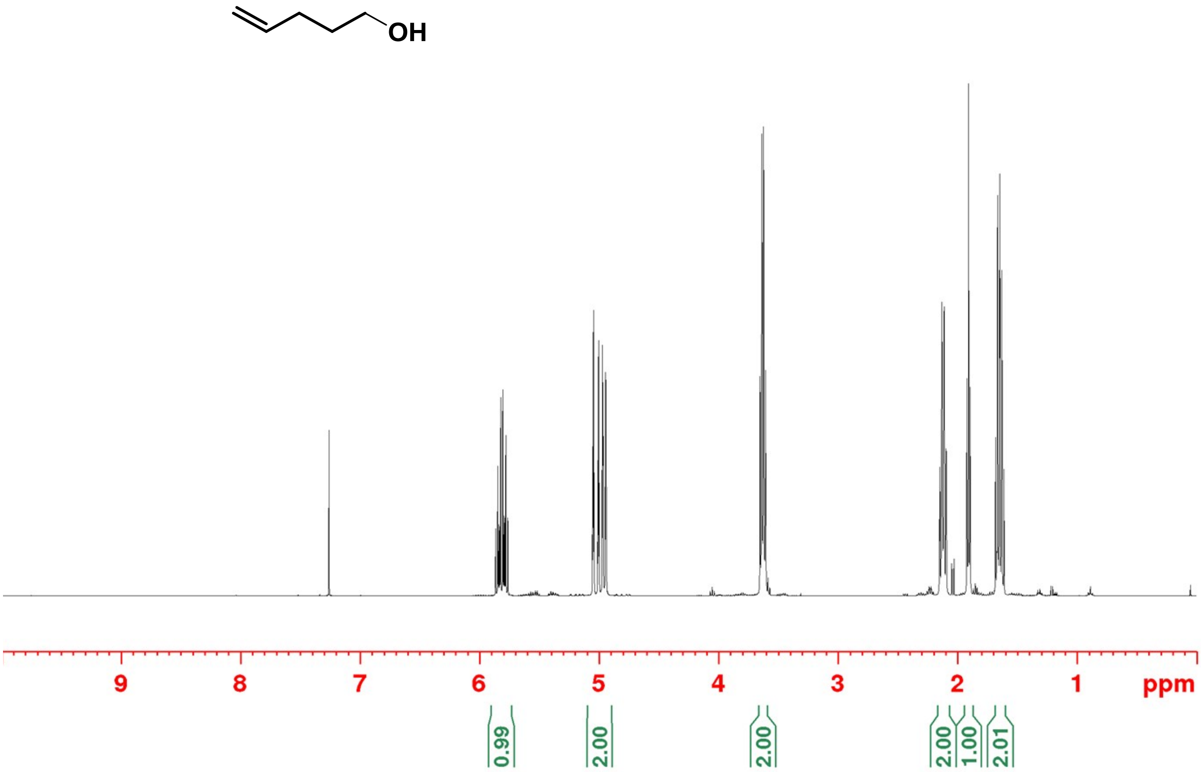
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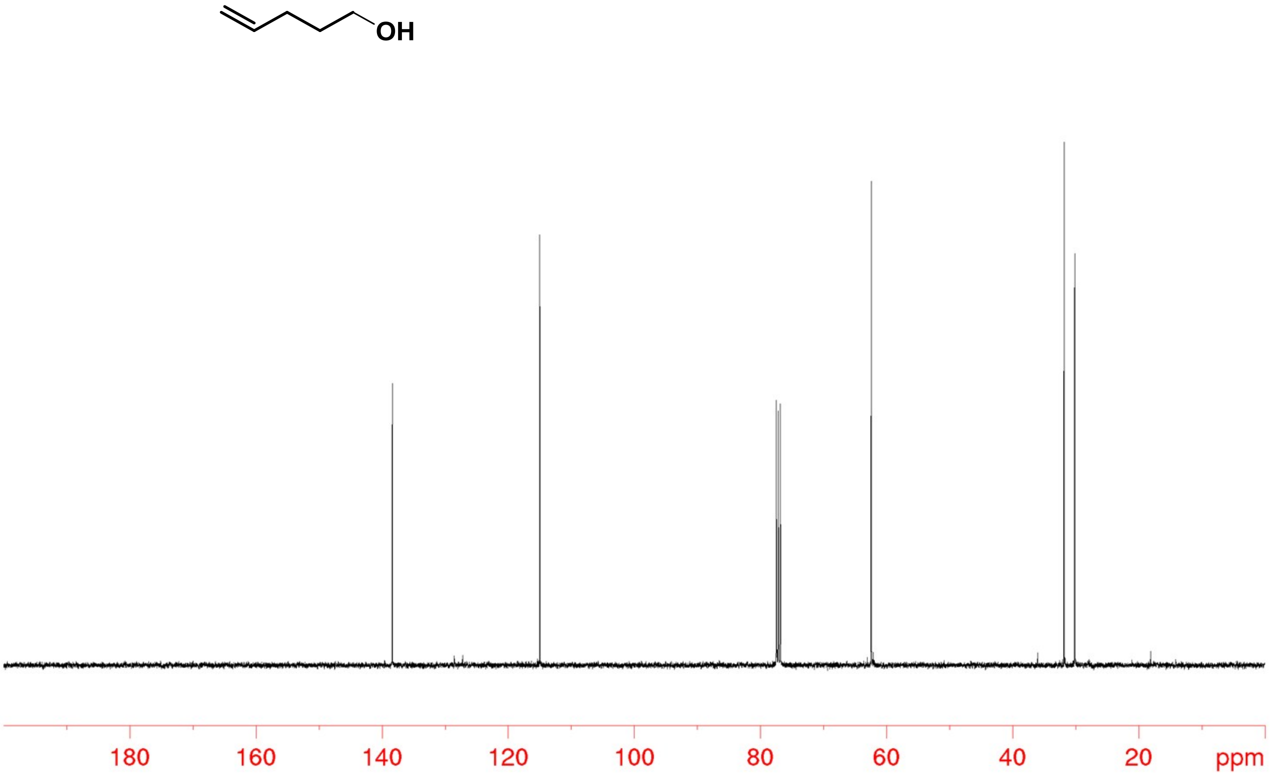
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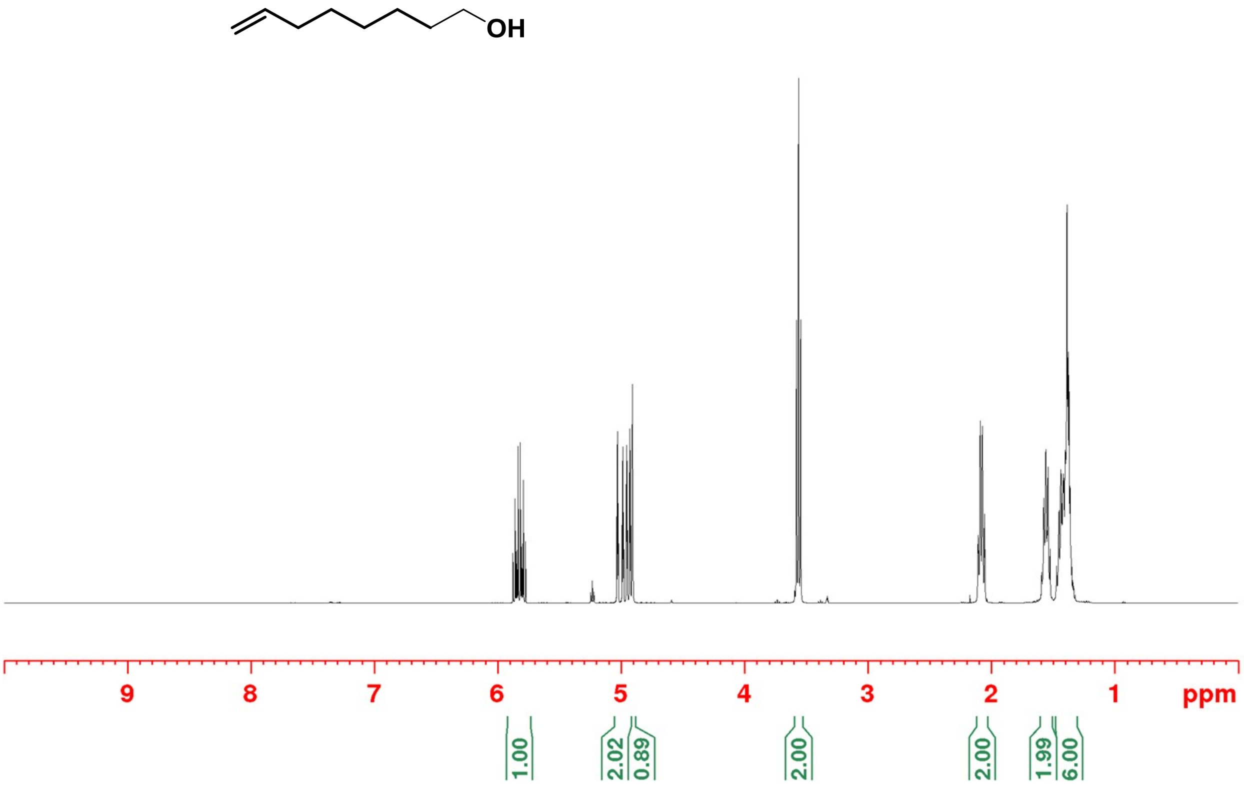
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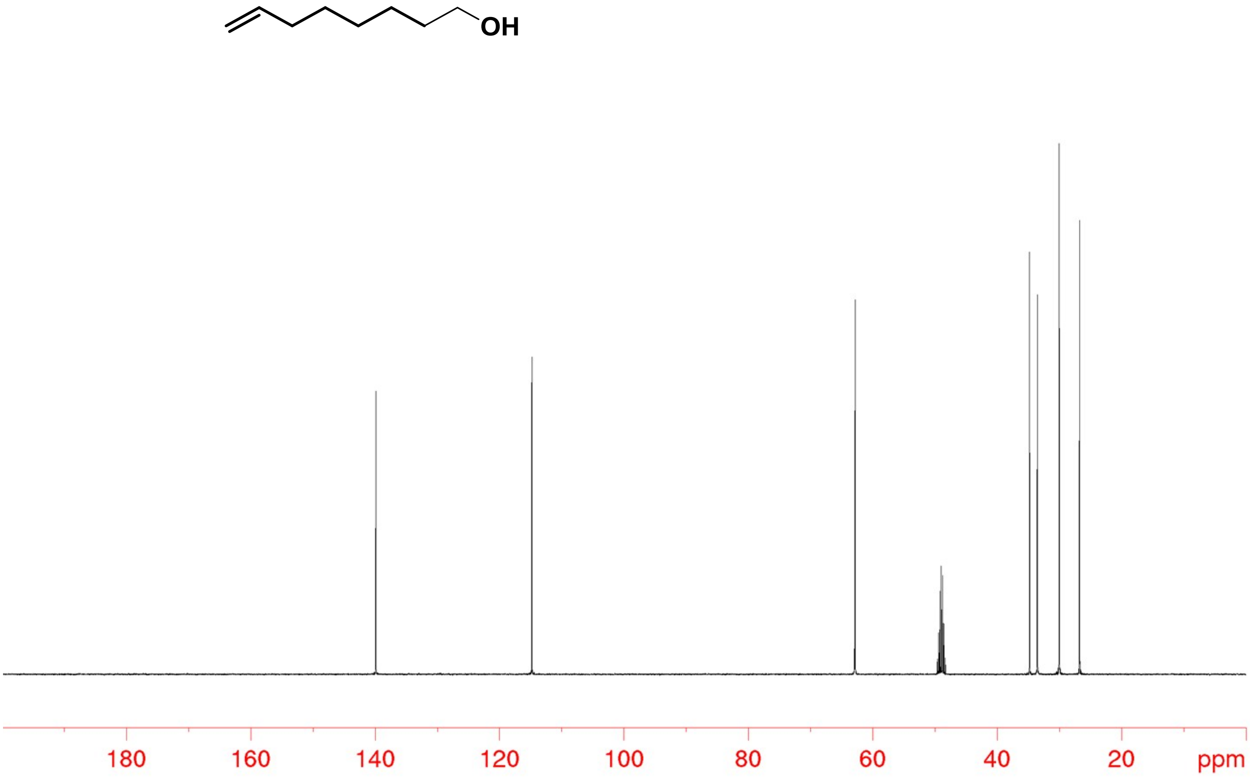
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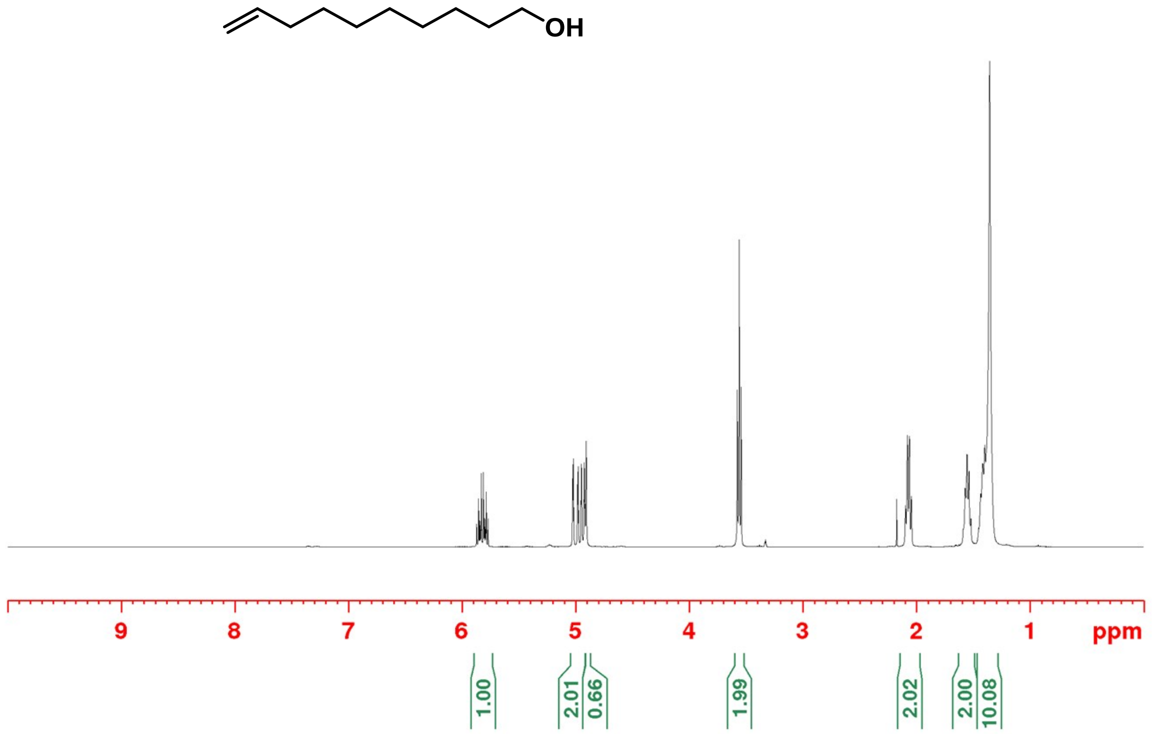
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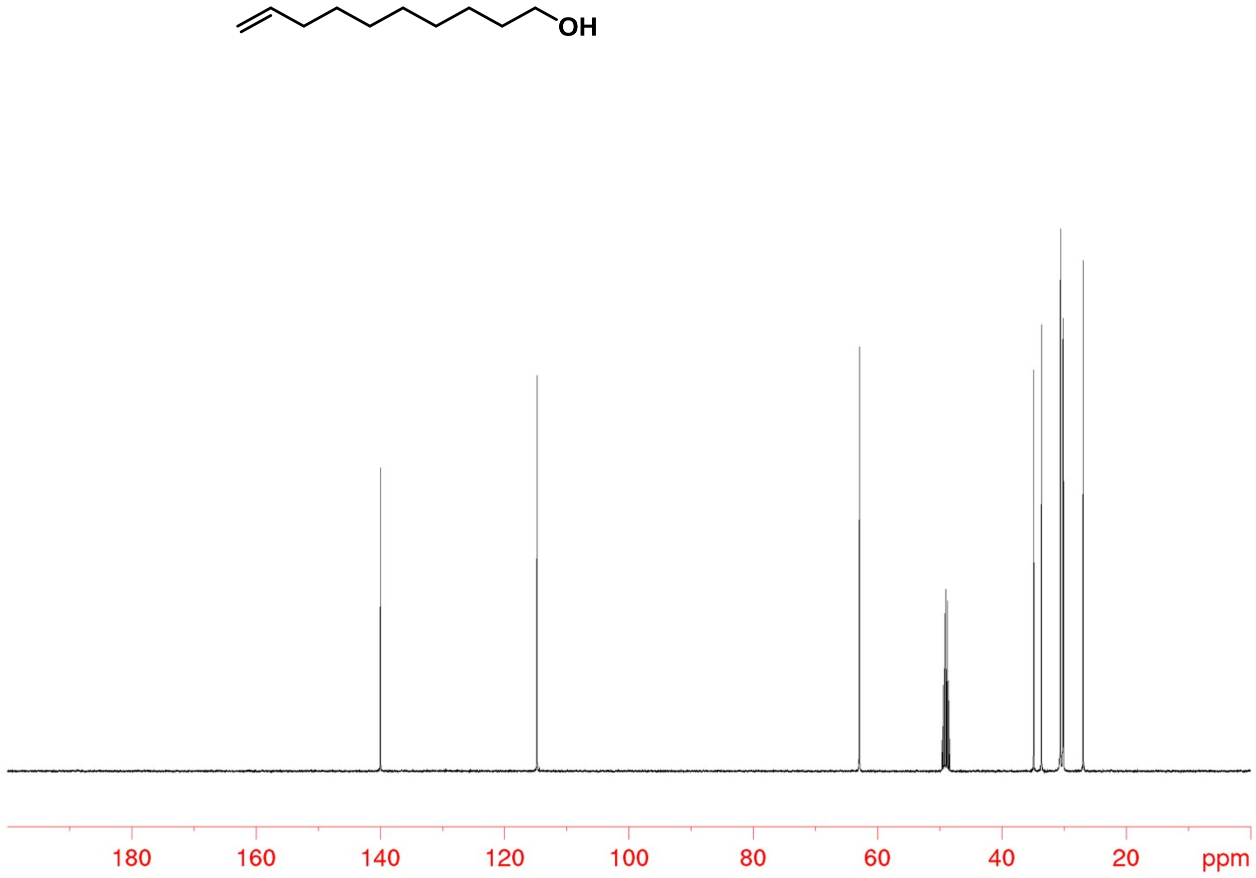
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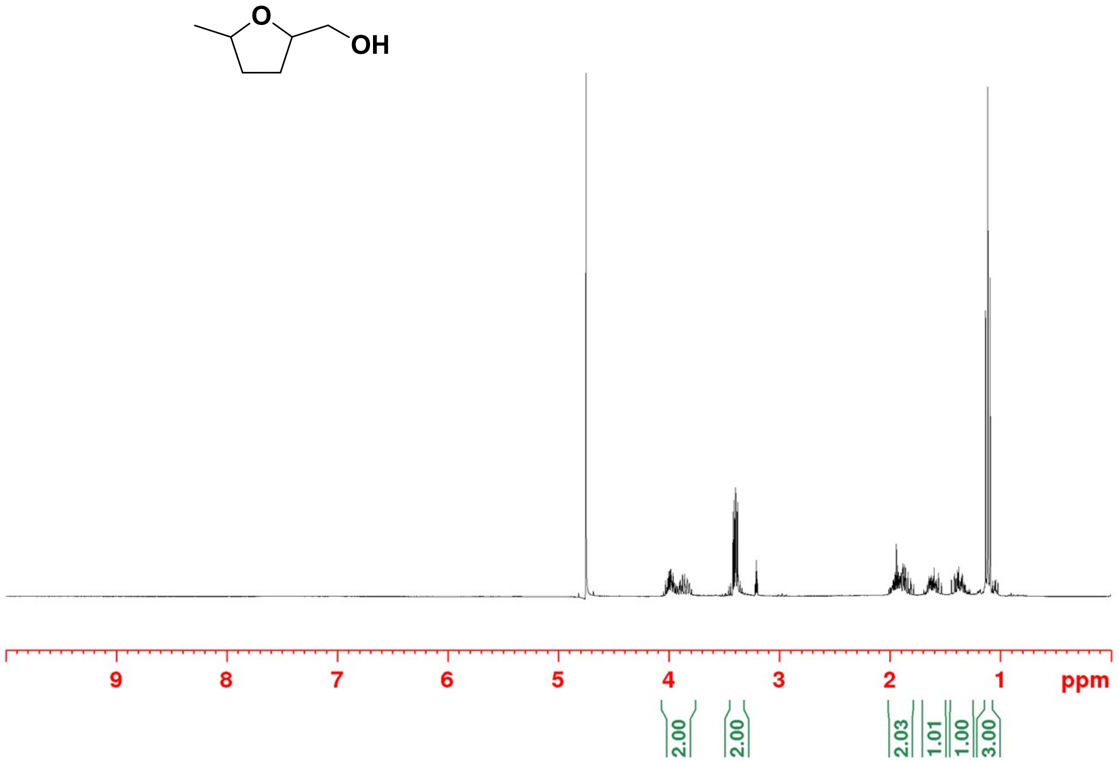

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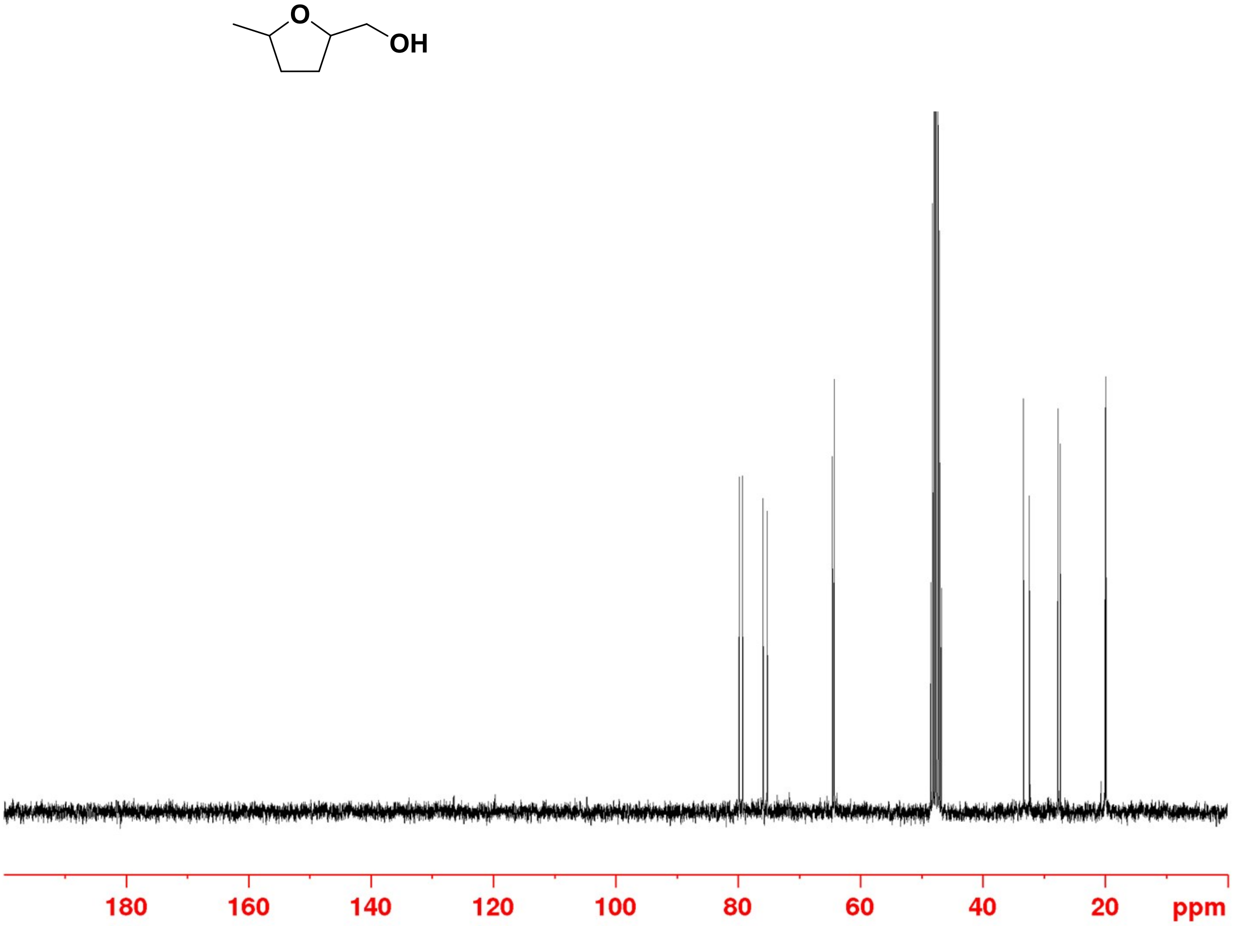

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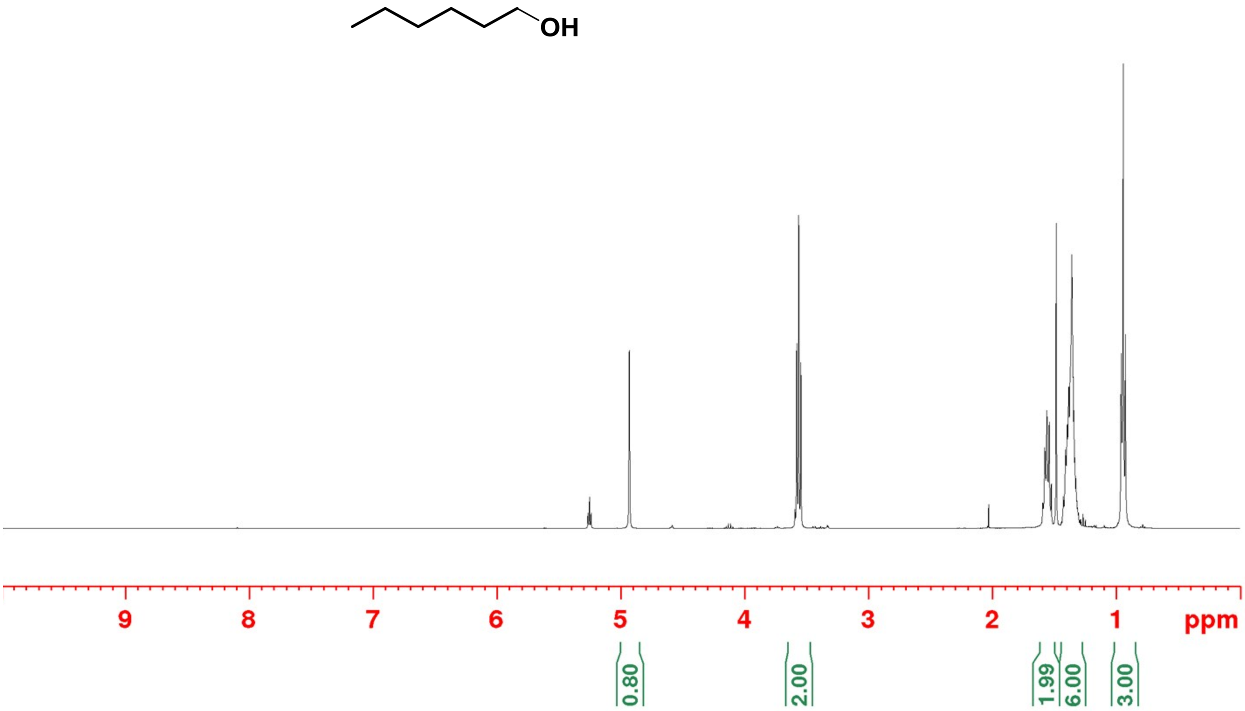
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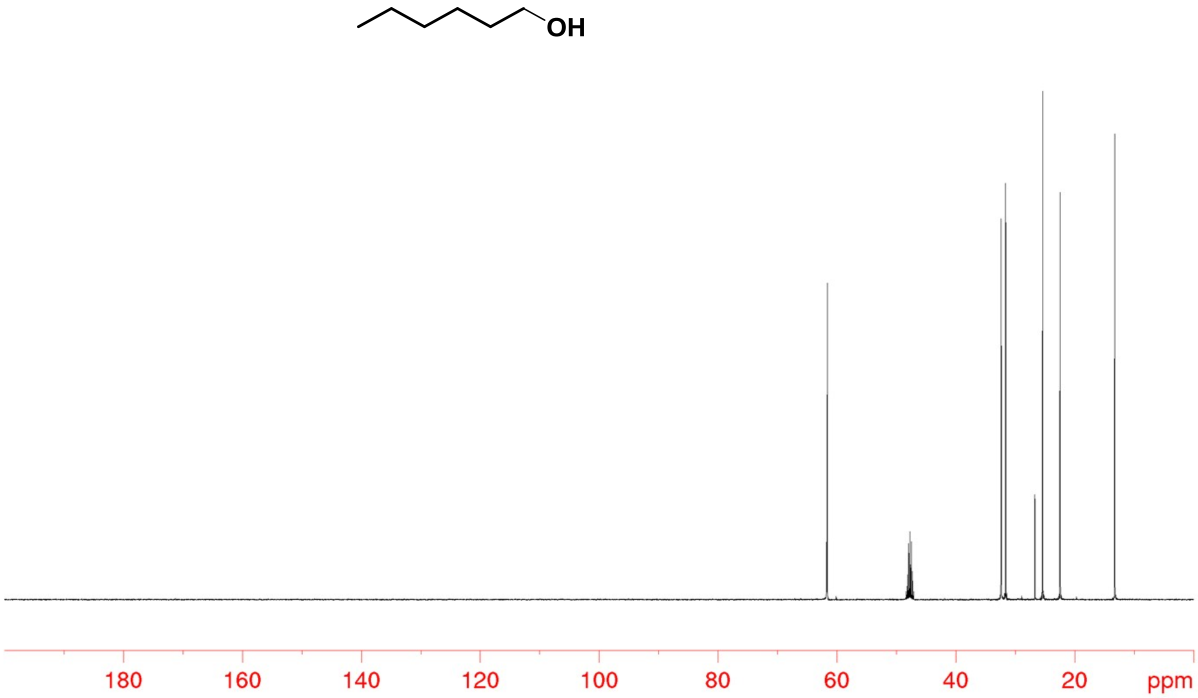
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